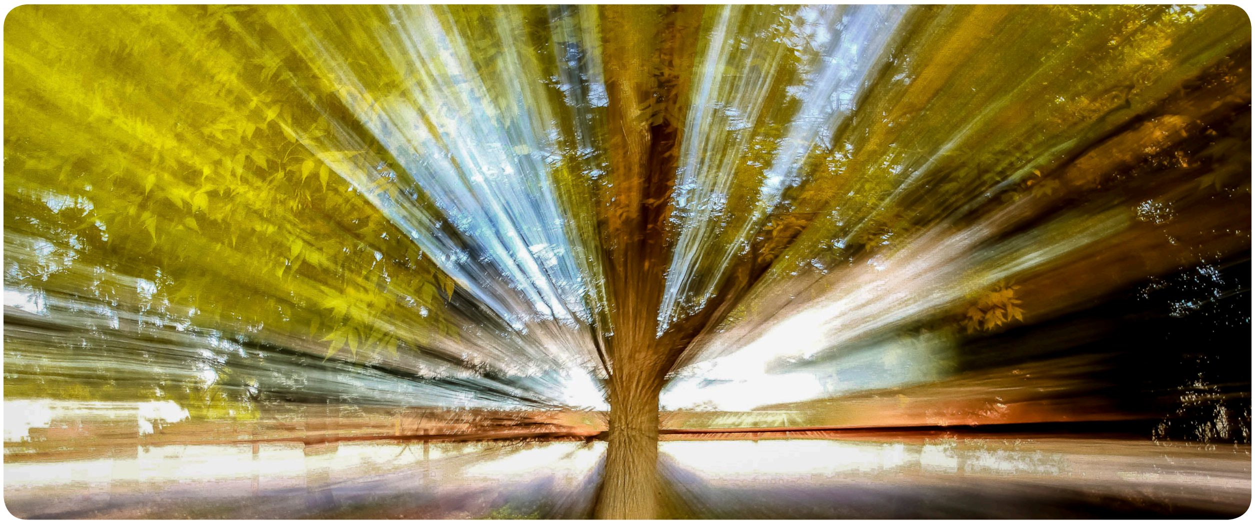
Cellulose Nano- and Micromaterial Production Study



Implementation Plan of the Yreka, California, Feasibility Analysis

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INTRODUCTION

Forest Service Research and Development (Forest Products Laboratory and Northern Research Station), the National Forest System (Pacific Southwest Region), and the U.S. Endowment for Forestry and Communities are collaboratively initiating a feasibility study for cellulose nanomaterial and micromaterial production in Northern California. The Yreka, California, site is characterized by wood species availability and water use constraints typical of western U.S. Government public lands and much of the Rocky Mountain region where forest product utilization options are limited.

Klamath National Forest, California.

THE ULTIMATE GOAL of the project is to develop a product option that can help fund forest management activities. A high-value product would support delivered timber costs sufficient to pay for harvesting and transportation costs for trees removed in forest restoration and hazardous fuel reduction operations.

OVERALL PROJECT GOALS

- Compare quality and particle characteristics for cellulose nanomaterials and cellulose micromaterials made directly from wood using six production methods
- Produce quantities of cellulose nano- and micromaterials sufficient to evaluate four applications
- Identify production site requirements (such as water use, water treatment) and evaluate these requirements relative to the Yreka location
- Determine production costs (capital and operating) for the cellulose nano- or microparticle intermediates

Supervisory Research Chemist Alan Rudie (left) tours Secretary of Agriculture Tom Vilsack (right) through FPL's nanocellulose pilot plant and shows nanocellulose samples.

This Public–Private Partnership will evaluate cellulose nano- and microparticle production options provided by one university, three private-sector companies, and the Forest Products Laboratory (FPL). Engineering evaluation referred to as AACE Class 5 (−30% to +40% capital costs) will be performed on each option and used to select one option for further analysis.

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BACKGROUND

Northern California and Southern Oregon are home to five National Forests (Klamath, Six Rivers, Rogue–Siskiyou, Shasta–Trinity, and Modoc National Forests) covering about seven million acres of U.S. Forest Service land. Yreka falls within Siskiyou County, currently a Federally designated HUB zone (Historically Underutilized Business zone) with a current unemployment of 12% and most recent job growth measure at –1.88%.

Ranging from very dry (average annual rainfall of 13 inches in the Medicine Highlands of the Modoc NF) to ample rain (80 inches in parts of the Six Rivers NF), the five forests represent a broad range of forest types and management needs. As with much of California and the Rocky Mountain states, few forest product options are available within reasonable transportation distance from the forests, and nearly all removals for fuels reduction and other management efforts have been funded from taxpayer dollars. This severely restricts the pace of the work needed to maintain forest health and protect communities from wildfire.

Cellulose nanomaterials have been known to exist for a half century but have received renewed attention because the tools and technologies to effectively measure, characterize, and utilize these and other nanodimensional materials have become commonly available only in the past 10 years. Cellulose nanomaterials are surprisingly strong (strength of steel at one-sixth the weight) and are expected to be affordable by competing material standards. The largest potential product volume is in composite products, including applications as varied as lightweight armor for military vehicles to car body panels to 100% renewable and compostable food storage containers. Other possible applications include support films for flexible electronics; very low density aerogel supports (to collect oil from environmental spills, provide high-surface-area support for chemical catalysts and battery electrodes, and for high-performance insulation products), and photo-electric applications (such as liquid crystal and piezo-electric applications).

The science surrounding production and use of cellulose nanomaterials has benefited greatly from technical interest in carbon nanotubes and similar inorganic nanoparticles, which have paved the way in terms of developing imaging techniques and surface compatiblization for composite applications. The two classic forms of cellulose nanoparticles—cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs)—have different potential uses. CNCs are chemically resistant nano-sized crystals of cellulose that exist in all cellulose products, including paper pulps and cotton. Although known since 1949, methods for larger scale production and industrial use have just been developed in the past decade and are not yet at a commercial level of readiness. CNCs are rigid rod-shaped particles and when produced from wood are about 6 nm in diameter and 100–150 nm long. They are the strongest form of cellulose nanoparticle and the form that exhibits both liquid crystal and piezo-electric properties. CNFs are string-like particles. A chemically produced form referred to as TEMPO oxidized cellulose nanofibrils (TOCNs) are particles 6–10 nm in diameter and 1–2 µm long, in linear or single-chain form. A variety of mechanical grades vary principally by type of chemical pretreatment and amount of subsequent mechanical energy required; this type is also long and filamentous, but the particles are cross-linked or branched, and particle diameters are in a broad range that can be as small as 6 nm and range up to 100 nm or more. Experience has shown that the benefits of smaller particle size usually plateau in the microparticle size range, and refining/grinding is usually terminated before true nano-scale (<100 nm) is achieved.

Research and development efforts to date have generally focused on materials produced from relatively pure cellulose sources or on processes that have first utilized a known laboratory cellulose isolation process before preparing the nanoparticles. The Yreka project intends to evaluate six cellulose nanoparticle production methods including CNCs (two methods), chemically prepared fibrils (two methods), and mechanically prepared fibrils (two methods), all produced directly from wood.

PRODUCTION METHODS

Cellulose nanocrystals utilizing the traditional sulfuric acid method

Forest Service R&D, Forest Products Laboratory

The basis for this method was discovered in 1949; current methods are based on a modified approach from 1953. A cellulose source is mixed into a sulfuric acid solution. The sulfuric acid dissolves and hydrolyzes the noncrystalline (amorphous) portion of the cellulose, leaving the crystalline regions as separate nano-scale particles that are decorated with sulfuric acid half-ester groups, which help to keep the particles apart and suspended in water. The method has about a 50% yield when starting from cellulose and is expected to have about a 25% yield starting from wood. The remaining cellulose (50%) and hemicellulose (25% of wood mass) will be hydrolyzed to simple sugars and abandoned in the process to simplify recovery of spent acid. Lignin will be an insoluble and nondispersed byproduct that can be isolated for other applications. The sulfuric acid production method is being commercially used by CelluForce in a 1-ton/day scale pilot plant in Windsor, Quebec, Canada, starting from bleached wood pulp.

Cellulose nanocrystals utilizing a peroxide radical chemical approach

Blue Goose Biorefineries, Saskatoon, Saskatchewan, and Pure Lignin Environmental Technology, Kelowna, B.C.

The process has two major components. First, the wood is converted to brown pulp with Pure Lignin Environmental Technology's patented two-step process of dilute nitric acid and ammonium hydroxide impregnation followed by alkaline extraction at atmospheric pressure. The washed pulp is then treated by the Blue Goose Biorefineries (BGB) process, which uses hydrogen peroxide and transition metal ions to both delignify wood and depolymerize cellulose. The crystalline regions are more resistant to the radicals produced by this chemical approach and remain after the other wood chemicals are rendered soluble by the treatment. Yield from wood is expected to be 25% to 35%. Lignin and hemicellulose side streams result from this process; among other market uses, Pure Lignin Environmental Technology has demonstrated their lignin as a polyethylene strength enhancer and their hemicellulose as a fertilizer and soil enhancer.

Cellulose nano-fibrils using a sulfur dioxide procedure

American Process Inc.

The American Process (API) production method involves both delignification of wood and carbohydrate hydrolysis using sulfur dioxide in ethanol, similar in some respects to the sulfite pulping process. The product can be either rod-shaped particles similar to the traditional cellulose nanocrystal, or string-like particles—cellulose nanofibrils. A unique advantage of the API process is that the lignin removed is recovered and can be used as an unreacted lignin, or can be re-deposited on the CN product to provide an interface between the CN particles and resin used in a composite product. API has recently started up a 0.5 ton per day facility in Thomaston, Georgia.

Cellulose nanofibrils using the TEMPO chemical pretreatment

Forest Service R&D, Forest Products Laboratory

Several research groups have evaluated the TEMPO treatment of wood particles, typically thermomechanical pulp. The processing conditions are nearly the same as required for TEMPO treatment of bleached wood pulp, but the sodium hypochlorite required are about three times what is needed for cellulose oxidation. Product yield is about 40% to 50% because nearly all the lignin and hemicellulose becomes soluble during the reaction. This reaction process offers no byproduct possibilities because both lignin and hemicellulose are highly degraded by hypochlorite and TEMPO oxidations. Effluent properties raise some concern because hypochlorite can produce polychlorinated phenols and other problematic chlorinated hydrocarbons. Oji Paper and Nippon Paper in Japan are currently pursuing small-scale demonstration of the TEMPO process starting from bleached wood pulp.

Cellulose microfibrils using mechanical pulping refiners

University of Maine

This process involves recirculating a wood pulp slurry through one or more modified disk refiners, similar to those conventionally used in the production of paper and paperboard. The process, which requires 20–30 passes though the refiner and at least one change in refiner plates, is normally continued until 90% of the fiber particles are less than 0.2 μm. Fibrils produced using this method are characterized by broader fiber diameter and length distributions than chemical-based methods. The fibrils appear to be branched in structure. The process is expected to work well with wood if the initial size of the wood particles is small enough so that they can be suspended in water and pumped through the refiner. Wood particles will be screened to remove dirt and reduce bark content. Overall yield from wood should be greater than 90%. The final product will be thickened to about 10% solids to minimize transportation costs and fresh water usage. This process has been piloted at the University of Maine using bleach kraft market pulp at the 1-ton/day scale. Southworth/Paperlogic has recently commissioned a 2-ton/day CNF production facility based on this technology at its specialty paper mill in Turners Falls, Massachusetts.

Microfibrillated cellulose/mineral composite material

FiberLean IMERYS

IMERYS has a proprietary process to manufacture commercial volumes of microfibrillated cellulose (MFC) suitable for use in a wide range of industrial applications. FiberLean is a composite product of MFC and mineral, with MFC content ranging widely depending on the application. The mineral, typically calcium carbonate or kaolin, plays an essential role in the transfer of mechanical energy to the cellulose fiber. The efficiency in processing allows the transformation from cellulose to MFC at a lower energy demand and with no additional chemicals compared with other processes.
Any water removed during the process can be reused with little to no treatment. Losses in the production process are extremely low, and the mineral portion of the product may offer some unique advantages to the end-use application, where downstream economies of manufacturing may be achievable; for example, kaolin and calcium carbonate are often used as components for reinforcing composite products.

ANCILLARY PRODUCT DEVELOPMENT ACTIVITIES

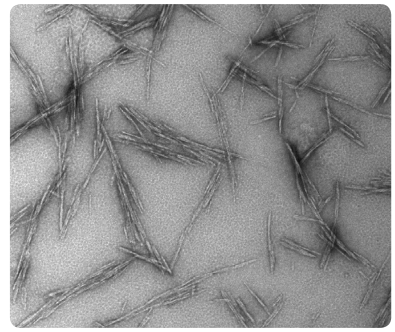
This project focuses on methods for producing cellulose nanoparticles as intermediates to be used in final products, so there will also be an emphasis on final product opportunities appropriate to the region.

The Yreka site raises specific local production constraints that need to be better understood and accounted for in Forest Service planning. The rural siting also raises specific product concerns.

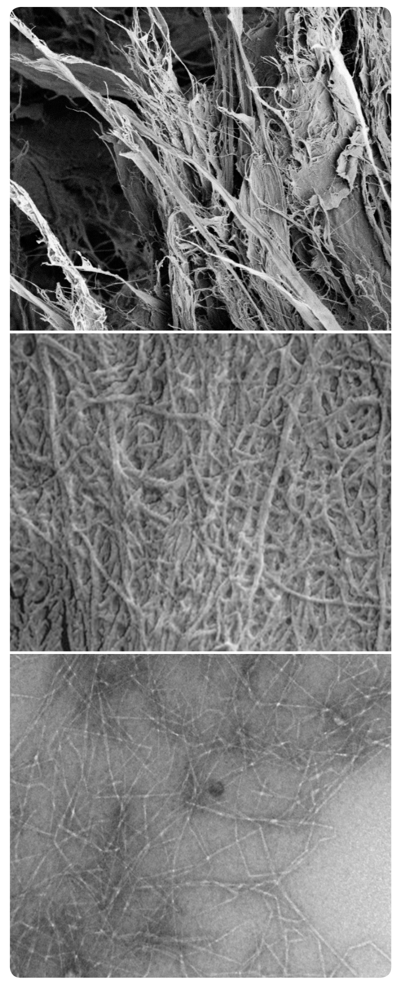
The project will evaluate the six process nanomaterial types in four potential product applications:

- reinforcing cement/concrete,
- a coating applied to preserve foods for shipping,
- a reinforcing fiber in polylactic acid, and
- the insulation core of structural insulated panels (SIPs).

To the extent necessary and appropriate, these evaluations will be built into the scope of work with the various participating cooperators.



Cellulose nanocrystals.



Cellulose nano-fibrils.

OPERATION AND GOVERNANCE

An operating board consisting of designated representatives from the Forest Service (Forest Products Laboratory, Northern Research Station, and Pacific Southwest Region) and the U.S. Endowment for Forestry and Communities will oversee and approve the work, approve budget allocations, review results, and make strategic decisions to achieve project goals. The operating board will meet regularly (no less than quarterly) via teleconference until the project is completed.

The Forest Service is providing the bulk of the funds, and several participants are also supplying resources.

The U.S. Endowment for Forestry and Communities will serve as a contractor to help manage funds, provide administrative support, and carry out subcontracting under the direction of the Forest Service.

PROJECT EXECUTION

Each participating organization will be provided with one or more wood sources from the Yreka area. They will each conduct necessary laboratory evaluations and then perform a large-scale experiment—preferably at pilot scale—that will be attended by a Forest Service engineer and a second industrial engineer contracted for this purpose.

At the end of the trial, the organization will submit a report that includes a detailed experimental description, with all chemicals and quantities used, and a block mass-balance diagram. Details will be sufficient to enable an engineering firm to develop an AACE Class 5 cost analysis of the method for a 100-ton/day plant located in the Yreka area and including all services needed by the proposed plant. The contract engineering company will provide a detailed list of what should be included in the report.

Organizations that are concerned about intellectual property and confidential business information will attach an appendix to their report identifying all intellectual property and business information in the report that they require to be held confidential. Although the initial reports are confidential, because public funds are being used, the Forest Service has a goal of publishing significant portions of each report and the Class 5 outcomes. The FPL will work with all cooperators to ensure that no confidential business information is disclosed. Forest Service R&D recognizes that corporate intellectual property and confidential business information must be preserved and that this may preclude publishing reports on some of the methods.

After the Class 5 studies are completed, one method deemed to be most appropriate for a more detailed analysis (AACE Class 4) will be selected by the Forest Service in consultation with the engineering company that performed the six Class 5 analyses. The Forest Service intends that the Class 4 outcome be made available to the public without disclosing any confidential business information that can be legally withheld. Should one of the corporate-sponsored methods be selected for the Class 4 analysis, intellectual property issues and publication concerns will be agreed to before initiating the Class 4 study.

If sufficient funds are available and a promising outcome results from the Class 4 analysis, a more detailed Class 3 analysis may be contracted.

TASK	RESPONSIBILITY	TARGET COMPLETION
PRODUCTION		
CNC (clean and slash chips)	FPL	4th quarter, 2015
CN (rods) (clean chips)	BGB	4th quarter, 2015
TEMPO CNF (clean chips)	FPL	4th quarter, 2015
Mechanical CNF (clean wood particles)	Univ. of Maine	4th quarter, 2015
Co-ground CNF (clean wood particles)	Imerys	4th quarter, 2015
CNC and CNF (clean chips)	API	4th quarter, 2015
ENGINEERING		
AACE Class 5	Harris Group*	1st quarter, 2016
Process selection	FPL/Harris Group*	1st quarter, 2016
AACE Class 4	Harris Group*	2nd quarter, 2016
Project decision	FPL	2nd quarter, 2016
AACE Class 3*	Harris Group*	3rd quarter, 2016

The Forest Products Laboratory's nanocellulose pilot plant in Madison, Wisconsin, is the first of its kind in the United States, situating FPL as the leading producer of domestic, renewable, forest-based nanomaterials. The plant can produce semicommercial-scale batches of cellulose nanofibrils and cellulose nanocrystals from renewable, wood-based sources.

This cellulose nano- and micromaterial production study is the next step toward using these materials in a more sweeping commercial basis.